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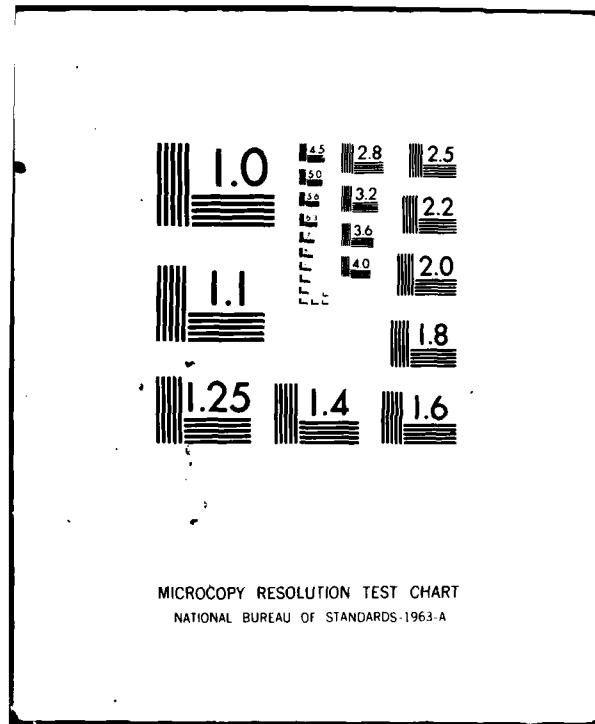
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polymeric reagent, catalyst activation, organometallic polymer hydrogenation, homogeneous catalysis, ion exchange, chlororhodium(I) tris(triphenylphosphine), silver(I) polystyrene sulfonate, dichlororuthenium(II) tris(triphenylphosphine), hydridorhodium(I) carbonyltris(triphenylphosphine), chlororhodium(I) ethylene-bis(triphenylphosphine), polystyrene bis(cyclopentadienyl)titanium dichloride,→

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Three different ways in which functionalized polymers can activate hydrogenation catalysts will be discussed. In the first example, a sulfonated divinylbenzene-crosslinked polystyrene is converted to a silver(I) salt. This silver(I) containing polymer selectively absorbs triphenylphosphine from solution in the presence of transition metal complexes. As a result of this removal of nonvolatile phosphine ligand, the activity of conventional homogeneous hydrogenation catalysts such as $((C_6H_5)_3P)_3RhCl$ or $((C_6H_5)_3P)_3Rh(CO)H$ can be

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POLYMER ACTIVATED CATALYSTS

by

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POLYMER ACTIVATED CATALYSTS

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Abstract

Three different ways in which functionalized polymers can activate hydrogenation catalysts will be discussed. In the first example, a sulfonated divinylbenzene-crosslinked polystyrene is converted to a silver(I) salt. This silver(I) containing polymer selectively absorbs triphenylphosphine from solution in the presence of transition metal complexes. As a result of this removal of nonvolatile phosphine ligand, the activity of conventional homogeneous hydrogenation catalysts such as $((C_6H_5)_3P)_3RhCl$ or $((C_6H_5)_3P)_3Rh(CO)H$ can be increased in cases where excess free ligand is known to lower catalytic activity. In a second example of polymer activation of hydrogenation catalysts we have shown that the hydrogenation activity of polystyrene supported bis(cyclopentadienyl)titanium dichloride is significantly altered when organomagnesium reagents instead of organolithium reagents are used to prepare an active catalyst. Rates of olefin isomerization of terminal alkenes to trans-2-alkenes and hydrogenation of terminal alkenes both are much faster with the organomagnesium reduced catalysts. Finally, transition metal complexes can be directly deposited on organometallic polymers to yield polymer supported heterogeneous catalysts whose activity in hydrogenation of terminal

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materials.

Introduction

The preparation of polymers capable of binding transition metal
compounds which are active homogeneous catalysts has been under de-
velopment for several years now. Examples of polymer supported cata-
lysts using many types of polymers and many different catalysts have
been described and reviewed.[1,2] The procedure of binding a homogene-
ous transition metal catalyst to a polymer has several important ad-
vantages. Succinctly, the advantages are that a polymer-supported
homogeneous catalyst offers the potential of being as selective and
reactive as its homogeneous counterpart while still providing the
experimental simplicity commonly associated with heterogeneous cata-
lysts. Polymer-supported catalysts are also beset by certain dis-
advantages. For example, polymer-bound transition metal complexes
are often found to be less active than their homogeneous counterparts.
Polymer-supported catalysts face disadvantages compared to typical
heterogeneous catalysts on refractory supports because of the prob-
lems of mass transport and heat transport associated with typically
used polymers. In addition, the experimental advantages of polymer-
supported catalysts (i.e. their recoverability) are sometimes offset
by slow leaching of the active (and often expensive) metal from the
polymer.

In this paper, we will be discussing some rather different ap-
plications of polymers in catalysis: the alteration of a homogeneous
catalyst's specificity on binding to a polymer; the activation of
conventional homogeneous catalysts using metal containing polymers;
and the use of organometallic polymers as precursors of highly dis-
persed heterogeneous catalyst species on an organic polymeric support.

Results and Discussion

<u>Polymer-Bound Titanium Alkene Isomerization Catalysts.</u> Typical procedures which emphasize the attachment of a homogeneous catalyst to a polymer proceed on the basis that the catalyst specificity of the polymer-supported catalyst will correspond to that of the homogeneous catalyst even if the activity is slightly altered. However, the potential of polymer-bound catalysts to catalyze reactions different from those catalyzed by their homogeneous counterparts has recently been recognized.[3] Here we describe our studies of the reactions of alkenes with reduced titanium species bound to polymers in which a significant alteration in the specificity of the catalyst is observed. In addition, our studies have shown a significant effect on catalytic activity results from changing the organometallic cofactor from an organomagnesium to an organolithium reagent.

The immobilization of bis(cyclopentadienyl)titanium dichloride on a polystyrene matrix was first described by Grubbs and Brubaker[4] who used this "immobilized" species to prepare an alkene hydrogenation catalyst whose activity was greater than its homogeneous analog. In this report we describe further examples of differences between catalysts derived from similar polystyrene-bound titanium species and their homogeneous analogs. In our studies we have shown that reduction of polystyrene-bound bis(cyclopentadienyl)titanium(IV) dichloride (1) with alkylmagnesium halides in ethereal solutions produces an alkene isomerization catalyst. We have also studied alkene hydrogenations using organomagnesium reduced 1 and its soluble analog as a further comparison to the organolithium-titanium(IV) systems. Although the exact nature of the catalytically active species could not be determined, ESR studies did establish that Ti(III) was a component, although not an active catalytic species, of these catalyst mixtures.

Originally we had hoped to prepare a polymeric version of the

titanium hydrometalation catalyst first described by Finkbeiner and Cooper (eq 1).[5,6] Indeed, while our studies were in progress cata-

$$RCH = CH_2 \quad \xrightarrow[\text{(CH}_3)_2\text{CHMgBr}]{\text{cat. Cp}_2\text{TiCl}_2} \quad RCH_2CH_2MgBr \qquad (1)$$
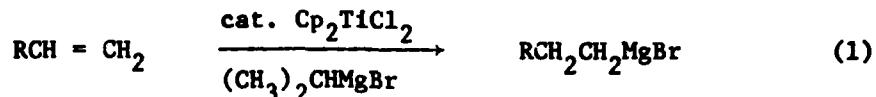
lytic hydroalumination of alkenes using the same polymer-bound catalyst we employed was reported.[7] However, when we attempted reaction 1 with polystyrene-bound bis(cyclopentadienyl)titanium dichloride we saw mainly alkene isomerization and little or no hydrometalation. These alkene isomerization catalysts were prepared either using a 2% divinylbenzene-crosslinked polystyrene support or a 20% divinylben-zene-crosslinked polystyrene support. Addition of excess alkylmagne-sium bromide or chloride to either polymeric titanium complex suspen-ded in ether resulted in a change in the color of either polymeric titanium complex from an initial red to black. The rate of the color change varied for different alkylmagnesium halides and corresponded roughly to the efficacy of the resulting isomerization catalyst (vida infra). Similar color changes were observed on addition of hydro-carbon solutions of n-butyllithium, sec-butyllithium, and tert-butyl-lithium. Grignard reagents without β-hydrogens (methyl, benzyl) also produced the same color change. The observed color changes were re-versible in that work-up using dilute HCl regenerated the polymers 1.

Addition of a terminal alkene to the catalyst prepared from 1 resulted in isomerization of the starting alkene (eq 2). This isomer-

$$RCH_2CH=CH_2 \quad \xrightarrow[\text{R'MgBr}]{\text{Ps-CpTi(Cp)Cl}_2} \quad RCH=CHCH_3 \text{ (mainly E)} \qquad (2)$$
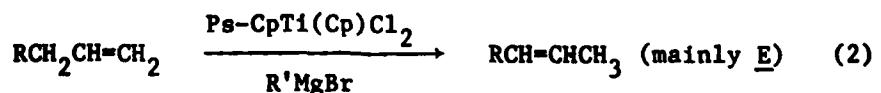
ization was successful with 1-butene, 1-pentene, and 1-octene. In-ternal alkenes such as 2-octene apparently do not further react. Similar behavior was noted in hydrogenation reactions.
In long term experiments in which fresh charges of Grignard reagent and starting alkene were periodically added, turnover numbers (total

mmol of alkene isomerized/mmol Ti) as high as 1000 were achieved. Less than 15% of the starting alkene formed alkane in contrast to the homogeneous reaction which produced 70% octane (by protonation on aqueous HCl work-up of an intermediate n-octylmagnesium halide) when 1-octene was allowed to react with isopropylmagnesium bromide and bis(cyclopentadienyl)titanium chloride under Finkbeiner and Cooper's conditions.[5,6]

The relative efficacy of various Grignard reagents for promoting the isomerization was tert-butyl > isopropyl > n-butyl. Methylmagnesium bromide and benzylmagnesium chloride were ineffective at generating an alkene isomerization catalyst. Typical product mixtures from these isomerizations were: 1-octene; E-2-octene (84%), Z-2-octene (12%), n-octane (4%); 1-butene; E-2-butene (72%), Z-2-butene (28%); 1-pentene; E-2-pentene (85%), Z-2-pentene (15%). The starting 1-alkenes were typically completely consumed. Alkyllithium reagents were ineffective at producing this isomerization catalyst although they are known to form alkene hydrogenation catalysts.[4]

Although we typically used gas chromatography to follow these reactions we also found ^{13}C NMR of sealed tubes containing substrate alkene, a Grignard reagent, and polymeric catalyst could conveniently be used to follow these reactions (Figure 1). In these experiments, the polymer and catalyst were not detectable because of the line broadening characteristic of solids. The substrate and product alkenes were, however, easily seen and their absorptions could be easily assigned. We believe this procedure could be generally useful in studying reactions involving polymer-bound catalysts so long as all substrates and reagents can be contained in an NMR tube and as long as the spectral analysis is simple.

The mechanism of alkene isomerization was not studied explicitly. However, a mechanism involving oxidative addition of an allylic C-H bond to titanium may be involved. This process is likely occur-
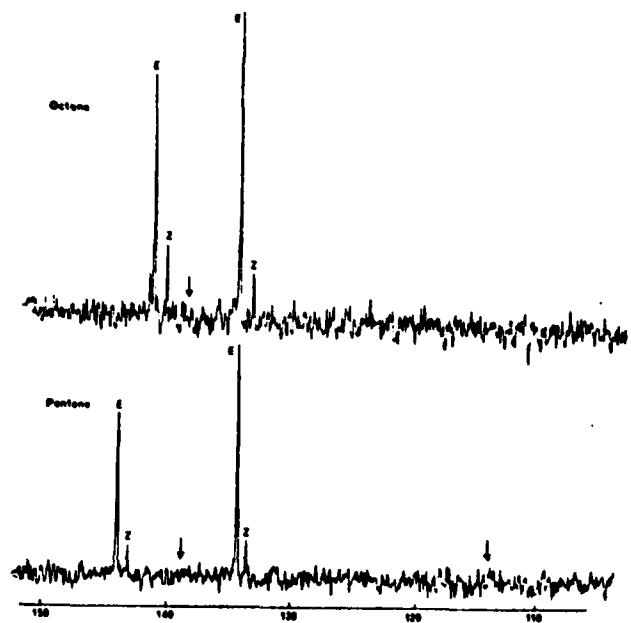
Figure 1. ^{13}C NMR spectrum of isomerization reaction. Arrows indicate position of resonances characteristic of starting 1-alkenes.

ring to a very limited extent for cyclohexene to give the small amount of benzene observed in attempted cyclohexene hydrogenations. Similar processes have been described for other metals.[7,8] The alternative process involving "Ti-H" addition and β elimination may also occur. A similar hydride addition-elimination seems likely to be occurring in the metalation reactions employing soluble Cp_2TiCl_2, isopropylmagnesium bromide and alkenes.[6]

Heterogeneous species such as the polymer-supported catalysts described above are not readily characterized except by analogy to homogeneous systems. Thus, we have been unable to further defing the actual catalyst. Nevertheless, our studies show that immobilization of homogeneous catalysts can achieve not only activation and experimental simplicity but also modified catalyst selectivity.

Polymeric Cofactors for Homogeneous Catalysts. A novel application of polymers in catalysis would be to use them to activate a conventional homogeneously catalyzed reaction. Instead of binding the catalyst to the polymer, the polymer in this operation would be used to selectively remove a catalyst inhibitor or poison. For many homogeneous transition metal catalysts the most active form of the catalyst results from a dissociation reaction like eq 3. The most active

$$ML_{n-1} \rightleftharpoons ML_{n-1} + L \qquad (3)$$
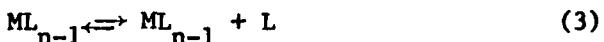
form of the catalyst in such a case, ML_{n-1}, is thus formed by an unfavorable equilibrium. Active catalysts may also be generated by oxidative addition of H_2 followed by reductive elimination of HX (eq 4). Decreasing the concentration of either L (eq 3) or HX (eq 4) would increase the concentration of the active catalyst species

$$MX + H_2 \rightleftharpoons MH_2X \rightleftharpoons MH + XH \qquad (4)$$

$$(X = halide, alkyl, aryl)$$
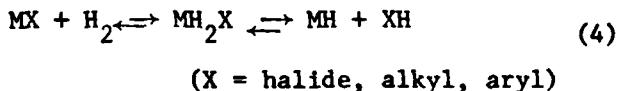
ML_{n-1} or ML according to Le Chatelier's Principle. Thus it might be possible to observe increased hydrogenation rates if suitable procedures for removing L or HX from a catalytically active system could be devised.

Our initial goal was to design a functionalized polymer to absorb a ligand L such as triphenylphosphine from an active catalytic system, in hope that the catalysis would then go more rapidly. The metal containing polymers described below meet this objective and do indeed accelerate alkene hydrogenations using some conventional homo-

geneous catalysts.

Other attempts to shift equilibria 3 and 4 have been made. One of the reasons $RhCl(PPh_3)_3$ was first supported on a polymer was in the hope of shifting equilibrium 3.[2,11] It was hoped that the concentration of ML_{n-1} could be increased. Several methods for removal of triorganophosphines from solution have also been tried. In 1970, an increased hydrogenation rate was claimed to be the result of reaction of a dissociated triorganophosphine, causing an equilibrium shift. The claim was not well substantiated.[12] In 1973 Knoth, Gosser and Parshall found that forcing solutions of PPh_3-containing platinum group compounds through a polyimide membrane separated the products of a catalysis and PPh_3 from the transition metal catalyst. This method requires pressures of several to 100 atmospheres and has also been effective for organometallic synthesis.[13,14] Shriver and co-workers have used soluble Lewis acids to react with the Lewis base PPh_3 to induce a faster hydrogenation rate.[15-17] However, the major rate increases seen were due to halide exchange or metal hydride formation. Many of the Lewis acids tried reacted with the catalyst and left it inactive. Shriver concluded that a ligand abstracting substance must be chosen with great care so that it will react with PPh_3 but not with the catalyst.

Our proposed scheme to remove triphenylphosphine ligand from a solution of a homogeneous catalyst required functionalized polymers. Specifically, we expected that Lewis acid containing polymers could be prepared which could discriminate between absorption of PPh_3 and a homogeneous transition metal catalyst. If a Lewis acid was supported on an insoluble polymer it would be expected to interact more rapidly with PPh_3 than with the larger transition metal catalyst because the pores in the polymer permit more rapid passage of smaller molecules. It is conceivable that the transition metal catalyst might not interact with the supported Lewis acid at all. The use of a polymer-supported cofactor to increase catalysis rates by absorption of free ligands is a novel application of polymers in transition metal chemis-

try. Such a ligand absorbing polymer would be expected to circumvent many of the side reactions encountered by Shriver.[15,17]

A polymeric reagent designed to absorb PPh_3 should meet several criteria. The polymer must not be catalytically active of itself, nor should it interact with the active catalyst. It should be easily prepared, preferably from commercially available materials if wide use is ever anticipated. It should be easily handled and, if possible, it should be air stable. The ability to absorb more than one type of ligand would also be advantageous.

Preparation of a polymeric reagent with these characteristics was successfully accomplished using commercially available ion exchange resins which had been exchanged with various metal salts. The ion exchange resin chosen as a support for preparation of ligand-absorbing polymers was Amberlyst 15,[18] a sulfonated polystyrene ($PS-SO_3H$). It is 20% crosslinked with divinylbenzene and has a pore size of 50-300Å. As a sphere of 20Å diameter may easily contain a molecule of PPh_3, there should be little problem with access of PPh_3 to the supported metal ion. Functionalization of $PS-SO_3H$ with metal ions was performed by conventional ion exchange techniques, and the efficacy of the resulting polymers for PPh_3 absorption was determined by monitoring the disappearance of PPh_3 from a PPh_3 solution which contained the solid $PS-SO_3M$ by ^1H NMR. The observed data for absorption of PPh_3 by several different $PS-SO_3M$'s is displayed in Table I. Silver(I)-exchanged $PS-SO_3H$ ($PS-SO_3Ag$) was clearly the most effective at removing PPh_3 from a 0.04 $\underline{M}$ solution of PPh_3 in THF; all the detectable PPh_3 was gone after 1 h.

An initial objective of our studies was to prepare a polymer which would be selective and absorb PPh_3 but not an active transition metal catalyst. The ability of $PS-SO_3Ag$ to selectively absorb PPh_3 has been shown by UV-visible spectroscopy. In these experiments, a toluene solution of $RhCl(PPh_3)_3$ was allowed to react with $PS-SO_3Ag$ and $PS-SO_3H$. The relative rates of absorption of PPh_3 and $RhCl(PPh_3)_3$

Table I. Absorption of Triphenylphosphine (PPh$_3$) by Metal-ion-exchanged Ion Exchange Resin (Macroreticular Sulfonated Polystyrene, Amberlyst 15).[a]

Metal Ion	%PPh$_3$ Absorbed
Co^{+3}	0
Co^{+2}	10
Ni^{+2}[b]	10
Cu^{+2}[b]	5
Cu^{+1}[c]	5
Ag^{+1}	100 (1h)

[a]Absorption occurring from a solution of PPh$_3$, 0.04 $\underline{M}$ in THF, after 12 h. [b]This resin also absorbed 10% of the P($\underline{n}$-Bu)$_3$ which was present in a benzene solution which was initially 0.4 $\underline{M}$ in P($\underline{n}$-Bu)$_3$. The solution turns yellow. [c]The copper was present as the amine complex.

by PS-SO$_3$H and PS-SO$_3$Ag were then determined spectroscopically. All concentrations were typical of catalytic conditions. The PPh$_3$ absorption was monitored at 262 nm and the RhCl(PPh$_3$)$_3$ absorption was monitored at 417 nm.

The absorbance at 417 nm was found to decrease slowly in the presence of both PS-SO$_3$H and PS-SO$_3$Ag; a more rapid decrease was found with PS-SO$_3$Ag. To an extent this decrease in absorbance reflects the differing ϵ for RhCl(PPh$_3$)$_3$ and [RhCl(PPh$_3$)$_2$]$_2$.[19] The dimer [RhCl(PPh$_3$)$_2$]$_2$ is reported to form slowly in non-polar solvents

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at these concentrations.[19-22] It was expected that dimer formation
would be accelerated by PS-SO$_3$Ag if this polymer were removing PPh$_3$.
The determination of relative rates for rhodium(I) absorption versus
PPh$_3$ absorption was therefore complicated by this dimerization reac-
tion which had the effect of reducing the apparent selectivity of
PS-SO$_3$Ag since dimer formation was not distinguished from RhCl(PPh$_3$)$_3$
absorption by UV-visible spectroscopy. Nevertheless, it was possible
to estimate that PPh$_3$ absorption was at least 10-100 times faster
than rhodium(I) absorption by this technique.

Having prepared the desired type of functionalized polymer, we
next set out to use it to accelerate catalytic reactions. However,
reactions in which RhCl(PPh$_3$)$_3$ only, RhCl(PPh$_3$)$_3$ and PS-SO$_3$H, or
RhCl(PPh$_3$)$_3$ and PS-SO$_3$Ag were used to hydrogenate the alkenes 1-oc-
tene, 1-hexene, cyclohexene, styrene, ethylacrylate and 1,5-cyclooc-
tadiene (1,5-cyclooctadiene was not hydrogenated) all occurred at the
same rate (Table II). Reaction rates were obtained by monitoring the
uptake of H$_2$ and plotting the data obtained as mmol of H$_2$ consumed/s.
The rate was determined by fitting a straight line to this data and
taking its slope. In the literature RhCl(PPh$_3$)$_3$-catalyzed alkene
hydrogenation rates have been reported to be reproducible to ±
10%.[10,21,23,24] James states that this reproducibility refers only
to the same catalyst sample and solvent batch.[25] Because of these
facts, a rate variation of ± 10% was not considered significant un-
less it was consistently repeated. The ineffectiveness of PS-SO$_3$Ag
under catalytic conditions apparently results from the inability of
PS-SO$_3$Ag to compete with other species in solution for free PPh$_3$.
However, PS-SO$_3$Ag is capable of PPh$_3$ absorption under hydrogenation
conditions. This was shown by hydrogenation reactions run in the
presence of excess PPh$_3$. When 0.01 to 0.02 $\underline{M}$ PPh$_3$ was present in
hydrogenations of styrene, 1-octene, and cyclohexene, the rates of
hydrogenation were from 1 to 13% of their uninhibited rates (cf.
Figure 2). Addition of PS-SO$_3$Ag produced a dramatic increase in the
rate of hydrogenation after an induction period of 350-1500 s; most

Table II. Hydrogenation of Alkenes by $RhCl(PPh_3)_3$ in the Presence of $PS-SO_3Ag$ and $PS-SO_3H$.[a]

Alkene	Cofactor	$[RhCl(PPh_3)_3] \times 10^3$, M	Rate $\times 10^3$ mmol H_2/s
Cyclohexene[b]	Nothing	2.23	1.50
Cyclohexene[b]	$PS-SO_3H$	2.11	1.30
Cyclohexene[b]	$PS-SO_3Ag$	2.21	1.48
1-Hexene[c]	nothing	3.01	1.00
1-Hexene[c]	$PS-SO_3H$	2.78	0.94
1-Hexene[c]	$PS-SO_3Ag$	2.89	1.04
Styrene[d]	Nothing	2.3	2.2
Styrene[d]	$PS-SO_3Ag$	2.3	2.2
Ethyl Acrylate[e]	Nothing	2.84	9.8
Ethyl Acrylate[e]	$PS-SO_3Ag$	2.73	9.8

[a]Run in 10 mL of toluene at 25°C. 0.20 g of $PS-SO_3H$ or $PS-SO_3Ag$ was used except as noted. [b]0.47 M. [c]0.20 M. [d]0.11 M. [e]0.23 M.

induction periods were about 700–800 s. The final hydrogenation rate achieved was comparable to the rate observed in the absence of any added PPh_3; when more alkene was injected after all the alkene initially present was consumed (about 2000 s), the hydrogenation rate was the same as that observed in the absence of any added PPh_3. By this time, virtually all of the excess PPh_3 had been adsorbed.

The polymeric reagent $PS-SO_3Ag$ clearly removes PPh_3 from organic solutions. The reason no catalyst activation was observed in Table II is apparently because $PS-SO_3Ag$ cannot compete with the other species in solution for free PPh_3 during a $RhCl(PPh_3)_3$ catalyzed hydrogenation. Therefore, if it were possible to "trick" $RhCl(PPh_3)_3$ into releasing PPh_3 while preventing dimerization, an increased hy-

drogenation rate might be observed.

This "trick" is indeed possible. The ethylene complex of RhCl-$(PPh_3)_3$, $RhCl(PPh_3)_2(C_2H_4)$ is known to form reversibly on exposure
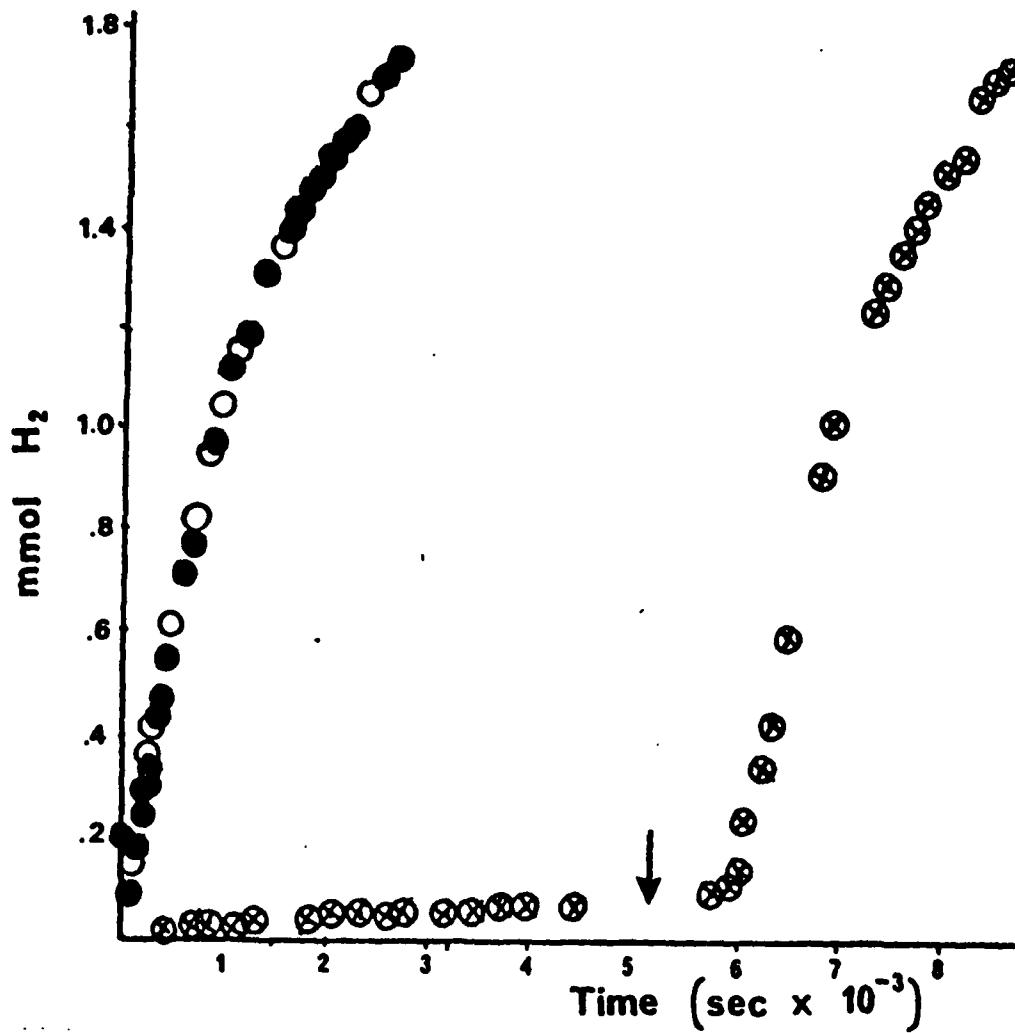
Figure 2. Hydrogenation of styrene (0.11 $\underline{M}$) catalyzed by 2.3 x 10^{-3} $\underline{M}$ $RhCl(PPh_3)_3$ in toluene at 25.0° in the absence of both PS-SO$_3$Ag and any excess PPh$_3$ (O), in the presence of PS-SO$_3$Ag (O), and in the presence of excess PPh$_3$ (1.6 x 10^{-2} $\underline{M}$ (⊗)). The effect of rate acceleration in the latter experiment reflects addition of PS-SO$_3$Ag at 5400 s (arrow in Figure).

of toluene solutions of RhCl(PPh$_3$)$_3$ to ethylene (eq 5).[26] If RhCl-

$$RhCl(PPh_3)_3 + C_2H_4 \rightleftharpoons RhCl(PPh_3)_2(C_2H_4) + PPh_3 \qquad (5)$$
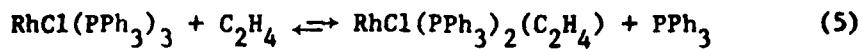
(PPh$_3$)$_3$ were dissolved in the presence of PS-SO$_3$Ag under an ethylene atmosphere, absorption of the PPh$_3$ released should drive eq 6 to the right, while still avoiding dimer formation. Subsequent addition of an alkene (after 900 s of mixing), removal of ethylene after 100 s by degassing, addition of hydrogen, and stirring then initiated the hydrogenation reaction. This procedure was found to have no effect on the rates of hydrogenation of styrene or ethyl acryate; these al-kenes were the most rapidly hydrogenated alkenes used in this study. However, 1-hexene, cyclohexene, and ethylene were observed to react

$$RhCl(PPh_3)_3 + C_2H_4 \rightleftharpoons RhCl(PPh_3)_2(C_2H_4) + PPh_3$$

$$\begin{array}{c}\text{add alkene} \\ \text{remove } C_2H_4 \end{array} \qquad \downarrow \qquad \begin{array}{c}\text{PS-SO}_3\text{Ag} \\ \text{absorbs}\end{array} \qquad (6)$$

$$RhCl(PPh_3)_2(\text{alkene})$$
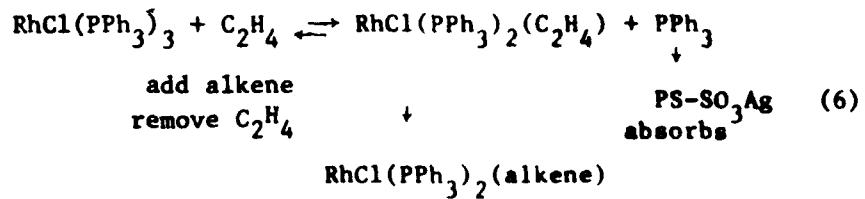
faster after ethylene pretreatment. Control experiments employing ethylene pretreatment in the absence of any cofactor, ethylene pre-treatment in the presence of PS-SO$_3$H, and no ethylene pretreatment or cofactor present, all resulted in the same unactivated rates.

·After an ethylene-pretreated hydrogenation of 1-hexene in the presence of PS-SO$_3$Ag, the PS-SO$_3$Ag residue was extracted with MeOH/ HNO$_3$. In this experiment the residue was rinsed three times with CH$_2$Cl$_2$ to remove any PPh$_3$ which might be clinging to the surface be-fore extraction by acidified MeOH. An absorbance maximum at 262 nm was observed by UV spectroscopy; this was the same as the maximum for PPh$_3$ in this solution. A spectrum of the acidified methanol-extract from a sample of PS-SO$_3$H showed no absorbance in this region. Thus PS-SO$_3$Ag does absorb PPh$_3$ when ethylene pretreatment is employed.

Further evidence that the concentration of RhCl(PPh$_3$)$_2$(alkene) has been increased by this ethylene pretreatment is found by comparing

the activations obtained in this study to work reported by Wilkinson in 1968.[27] The catalyst $RhCl(PPh_3)_n$ (n = 2,3) was formed in situ by combination of varying ratios of PPh_3 and $[RhCl(COD)]_2$ with alkene under H_2. These reactions were run at rhodium and alkene concentrations comparable to those used in this work; a rate enhancement of 1.4 for hydrogenation of 1-hexene was observed for n = 2 as opposed to n = 3. This compares with the twofold rate enhancement seen in this work following ethylene activation in presence of $PS-SO_3Ag$, as opposed to an unmodified hydrogenation using $RhCl(PPh_3)_3$. The similarity of these results suggests that the concentration of $RhCl(PPh_3)_2$ is indeed increased when ethylene pretreatment is employed in presence of $PS-SO_3Ag$.

The idea of shifting equilibrium 3 or equilibrium 4 using a polymeric reagent should be generally applicable. As was described above $PS-SO_3Ag$ is a suitable species for absorption of PPh_3. This polymer was therefore also examined as a means of activating other common homogeneous catalysts.

In the absence of any cofactors, $RuCl_2(PPh_3)_3$ is not a good alkene hydrogenation catalyst for 1-hexene or cyclohexene in toluene.[10] Hydrogen uptake occurred very slowly, at a rate of about 4 x 10^{-4} mmol H_2/s. However, if $PS-SO_3Ag$, $PS-SO_3H$, neutral alumina, $PS-CH_2NMe_3(OH)$ (Dowex 21K) or DMF were added to the solution containing $RuCl_2(PPh_3)_3$, the solution gradually turned from brown to red over a period of about 200 s. The hydrogenation rate increased dramatically; H_2 uptake occurred up to 15 times faster after the introduction of the cofactor (Table III). However, the use of polyethylene or macroreticular styrene did not lead to any rate enhancement or color change. Separate experiments showed each cofactor which produced rate enhancements to be capable of absorbing HCl. Only $PS-SO_3Ag$ absorbed PPh_3.

The increase in the alkene hydrogenation rate which followed the addition of an HCl absorbing cofactor to a solution of $RuCl_2(PPh_3)_3$

Table III. Acceleration of 1-Hexene Hydrogenation by $RuCl_2(PPh_3)_3$ Using Various Cofactors.[a]

Rate x 10^3, mmol H_2/s	Cofactor
0.36	Nothing
5.6	PS–SO$_3$Ag
2.7	PS–SO$_3$H
2.1	PS–SO$_3$Na
1.2	PS–CH$_2$H(CH$_3$)$_3$(OH)
5.5	Neutral alumina
1.8	Polyethylene
0.24	Polystyrene, macroreticular
0.26	

[a]In toluene, 10 mL, at 25°; [1-hexene] = 0.73 $\underline{M}$; [$RuCl_2(PPh_3)_n$] = 3.6 x 10^{-3} $\underline{M}$. The rates were determined from data collected from 200–800 s.

and 1-hexene under H_2 is consistent with conversion of at least some of the $RuCl_2(PPh_3)_3$ present to $RuHCl(PPh_3)_3$ by absorption of HCl (HX in eq 4). The hydrogenation rates obtained in this work are almost an order of magnitude smaller than those obtained for dilute (<10^{-3} $\underline{M}$) solutions of $RuHCl(PPh_3)_3$.[10,29] The relatively depressed hydrogenation rates observed in this work are consistent with the incomplete conversion of $RuCl_2(PPh_3)_3$ to $RuHCl(PPh_3)_3$ as was shown by subsequent ^{31}P [^1H] NMR experiments.

When PS–SO$_3$Ag was present in a solution of $RuCl_2(PPh_3)_3$ and 1-hexene, the initial hydrogenation rate was about two and a half times faster than when PS–SO$_3$H was present. Although these rates tended to decrease after about 1000 s, this may be due to alkene consumption rather than catalyst deactivation. Hydrogenation rates

in the presence of PS-SO$_3$H and RuCl$_2$(PPh$_3$)$_3$ also tended to decrease after about 3.8 mmol (48%) of the 1-hexene initially present was consumed. This rate differential suggests that PS-SO$_3$Ag is a more efficient HCl absorber than PS-SO$_3$H, or that the PPh$_3$ absorption occurring in the PS-SO$_3$Ag experiment may be important. It is thus possible that the presence of PS-SO$_3$Ag may activate RuCl$_2$(PPh$_3$)$_3$ by absorption of both HCl and PPh$_3$. This conclusion was supported by the results of GC analysis of a 1-hexene hydrogenation using RuCl$_2$(PPh$_3$)$_3$ as the catalyst precursor and either PS-SO$_3$Ag or PS-SO$_3$H as the cofactor which was stopped after 500 s. The reaction mixture was analyzed for hexane and hexenes. When PS-SO$_3$H was the cofactor, 83.3% of the 1-hexene initially added had been converted to hexane; 15.6% was still 1-hexene, 0.01% was 3- or trans 2-hexene, and 1.1% was cis 2-hexene. However, when PS-SO$_3$Ag was the cofactor, more isomerization had occurred. The six-carbon species were distributed: hexane, 79.1%; 1-hexene, 17.0%; 3- and trans 2-hexene, 2.0%, and cis 2-hexene, 1.8%. While isomerization is slight in each case, there is approximately three times as much isomerization when PS-SO$_3$Ag is used as the cofactor. The great selectivity exhibited by RuHCl(PPh$_3$)$_3$ for 1-alkene hydrogenation is considered to be a result of steric hindrance from the three PPh$_3$'s associated with the molecule. This also makes isomerization difficult as there is not enough room to accommodate an internal alkene easily. Thus, removal of PPh$_3$ from solution would be predicted to increase the isomerizing ability of this catalyst, as it appears to have done. A related experiment was the hydrogenation of an internal olefin, cyclohexene, in presence of RuCl$_2$(PPh$_3$)$_3$ and PS-SO$_3$H or PS-SO$_3$Ag. As stated above, RuHCl(PPh$_3$)$_3$ is not an efficient hydrogenation catalyst for internal olefins.[29] Formation of RuHCl(PPh$_3$)$_2$ might be expected to result in a faster rate for cyclohexene hydrogenation. The addition of PS-SO$_3$H to a solution of RuCl$_2$(PPh$_3$)$_3$ and cyclohexene under H$_2$ led to a five-fold rate increase for the extremely slow hydrogenation. The addition of PS-SO$_3$Ag resulted in a rate nine times faster than that observed in the absence

of any cofactor; nonetheless, the rate was still extremely slow. Although there are numerous other catalysts which are more efficient for this type of hydrogenation, absorption of PPh_3 by $PS-SO_3Ag$ does seem to be significant in inducing a faster hydrogenation rate for an internal olefin.

Dissociation of phosphine is regarded as essential to the mechanism generally accepted for many homogeneous hydrogenations of alkenes which are catalyzed by phosphine-containing transition metal compounds.[10] Thus several other common hydrogenation catalysts were surveyed to look for possible activation in the presence of $PS-SO_3Ag$. A brief account of these reactions is provided below.

Hydrogenations using $RhH(CO)(PPh_3)_3$[30-32] were run as follows: the catalyst was dissolved in toluene or THF in presence of $PS-SO_3Ag$ and stirred for a total of 1200 s, at which point alkene was injected. Rates of hydrogenation of 1-hexene, 0.31 $\underline{M}$, were the same regardless of the presence of $PS-SO_3Ag$. This was true at catalyst concentrations of both 1.3×10^{-3} $\underline{M}$ and 6.0×10^{-3} $\underline{M}$. However, styrene (0.2 or 0.6 $\underline{M}$) is hydrogenated about 10 times more slowly than 1-hexene.[33] It was hydrogenated about 30-60% faster in presence of $PS-SO_3Ag$ when $RhH(CO)(PPh_3)_3$ concentrations of 3×10^{-3} $\underline{M}$ to 10×10^{-3} $\underline{M}$ were employed; however, at 0.9×10^{-3} $\underline{M}$ in $RhH(CO)(PPh_3)_3$, no rate enhancement was observed.

The major interaction of $RuCl_2(PPh_3)_3$ with $PS-SO_3Ag$ and $PS-SO_3H$ under homogeneous hydrogenation conditions was HCl absorption by the polymer (vida supra). A similar system, $RuH(OAc)(PPh_3)_3$, which was not susceptible to this reductive elimination, was therefore chosen so that PPh_3 absorption could be studied.[34]

Hydrogenations of 1-hexene in THF were observed to occur 1.4 times more quickly in presence of $PS-SO_3Ag$. Addition of $PS-SO_3H$ has been observed to result in a slower rate of hydrogenation, 0.2 times the rate observed in the absence of any cofactor. This deactivation may have resulted from attack on the carboxyl group by the supported

acid. The question was not pursued. The presence of PS-SO$_3$Ag also led to an increase in the rate of styrene hydrogenation catalyzed by RhH(OAc)(PPh$_3$)$_3$ in THF, by a factor of 1.5 to 1.8. Cyclohexene was not detectably hydrogenated by RhH(OAc)(PFh$_3$)$_3$ in the presence or the absence of PS-SO$_3$Ag.

In summary, the polymer PS-SO$_3$Ag has been shown to be effective at inducing a rate acceleration for alkene hydrogenation in many PPh$_3$-containing systems. It was not effective at inducing a rate acceleration in all hydrogenations studied. Selective absorption of either L or HX in eq 3 and 4 was demonstrated. It seems likely that other suitably designed polymers could also be prepared which might demonstrate these effects. Alteration of the polymer's functionality or structure could increase the activity and selectivity of these polymeric cofactors.

Dispersed Metals on Polymers. In recent work we have succeeded in developing routes to a variety of organometallic polymers containing reactive groups.[35,36] These organometallic polymers or those developed by other groups provide a way of preparing new organometallic polymers from the catalytically active Group VIII metals according to eq 7. When reactive organometallic polymers such as lithiated

$$\text{Polymer-metal} + \text{MCl}_n\text{L}_m \longrightarrow \text{Polymer-MCl}_{n-1}\text{L}_m + \text{Metal-Cl} \quad (7)$$
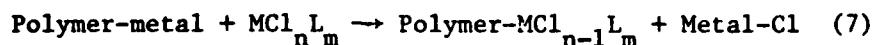
polystyrene are allowed to react with palladium(II) salts in reactions like 8 and 9, organometallic polymers are expected to be formed which are functionalized with highly dispersed palladium complexes. Subsequent thermolysis or reduction can transform these palladium(II) species into palladium(0) which can then be used as active alkene and alkyne hydrogenation catalysts. Palladium(0) aggregate size variations and surface areas for the resulting heterogeneous catalysts may

$$\text{PS-Li} + (\underline{n}\text{-Bu}_3\text{P})_2\text{PdCl}_2 \longrightarrow (\text{PS})_n\text{-PdCl}_{n-1}(\text{P}\underline{n}\text{-Bu}_3)_2 \quad (8)$$

$$\text{PS-Li} + (\text{COD})\text{PdCl}_2 \longrightarrow \text{PS-Pd}(0) \quad (9)$$
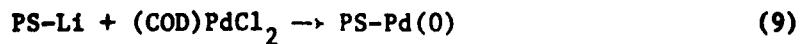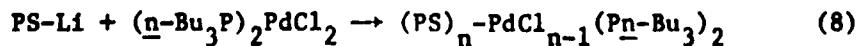
be determined from electron micrographs. Two representative micrographs are shown in Figure 3.

The activity of these heterogeneous catalysts toward terminal and internal alkenes is comparable to palladium-on-carbon catalysts as shown by the data in Table IV. Greater selectivity than Pd/C for terminal versus internal alkene hydrogenation was seen. Alkynes were

2000 Å

1000 Å
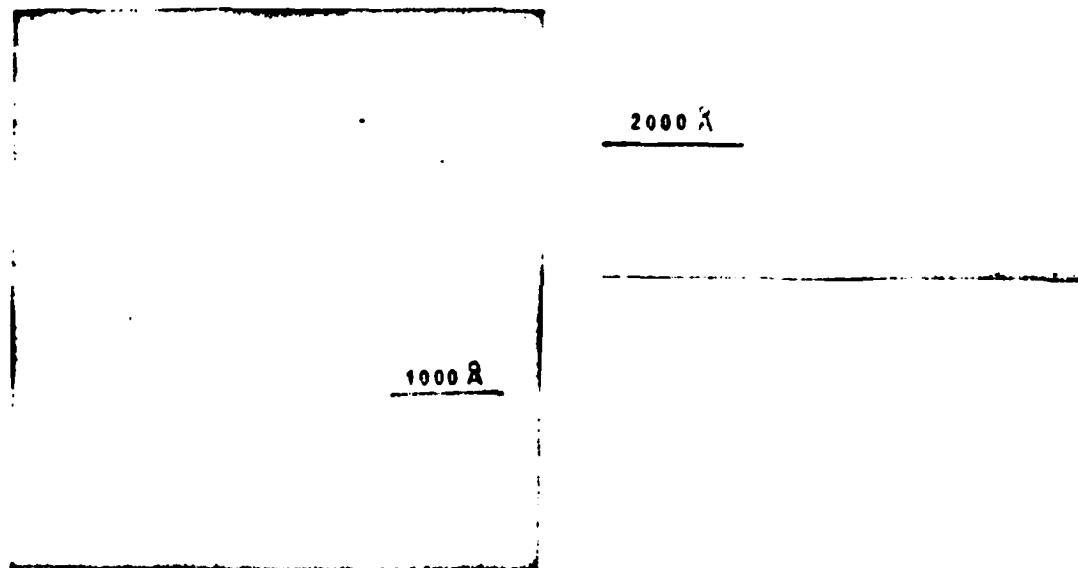
Figure 3. Electron micrographs of polystyrene-palladium(0). Metal aggregates range in size from 10-40Å and are localized along the polymer pore surface.

preferentially hydrogenated in the presence of alkenes, and as a result, alkenes could be isolated in high yield after the addition of one equiv of hydrogen. Alkene isomerization was competitive with hydrogenation in cases where more substituted alkenes could be formed. For example, after the partial hydrogenation of 1-hexene, the reaction solution contained 1-, 2-, and 3-hexene and n-hexane.

Table IV. Hydrogenation Reactions Using Polystyrene-Palladium(0).[a]

Catalyst[b]	Hydrogenation Rate (mmol H_2/min-mmol Pd)	Substrate
(n-Bu$_3$)PdCl$_2$ (0.4% Pd)	2.4	1-Octene
"	0.4	Cyclohexene
(COD)PdCl$_2$ (1.26% Pd)	6.1[c]	1-Octene
"	6.7	Cyclohexene
"	34.7	1-Octyne
1% Pd/C	26.8	1-Octene
"	20.8	Cyclohexene
"	22.8	1-Octyne
5% Pd/C	35.8	1-Octene
"	14.0	Cyclohexene
"	79.0	1-Octyne

[a]Hydrogenations were performed at 1 atm pressure and room temperature with 0.05-0.5 g of catalyst and 10 mL of THF which was 0.2 $\underline{M}$ in substrate. Rates were followed using a gas buret. [b]The indicated palladium complexes were allowed to react with lithiated polystyrene and reduced. [c]Whole polymer beads. Ground beads hydrogenate octene at 48.7 mmol H_2/min-mmol Pd.

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